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(54) Battery separator containing aromatic additive

(57) Battery separators made primarily from an olefinic polymer, especially polyethylene, are protected from oxidative attack by incorporation therein of, or coating with, an oil having an aromatic content of 40% or more by weight.

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SPECIFICATION

Battery separator containing aromatic additive

This invention is concerned with battery separators having as a primary structural material an olefinic polymer. Battery separators of this kind, when subjected to substantial oxidative attack, lose so much of their physical strength that their life and therefore the life of the battery are shortened. While these polymers tend to be resistant to the acids or alkalis employed in batteries, they are not totally resistant over normal battery life.

The present invention provides a way of extending the useful life of the above type of battery separator. The separator of the invention comprises an olefinic polymer and between about 5 and about 25% of the weight of the battery separator of an aromatic oil, having an aromatic content of 40% by weight. An important factor in the present invention is that the aromatic oil does not impart any substantial direct damage to the electrical resistance properties of the separator and, in the preferred ranges in particular, has been found inexplicably to improve them.

U.S. Patent 3,351,495 teaches the use of plasticizers including oil in the manufacture of battery separators having polyolefins as a primary structural material—see the bottom of Col. 4 and top of Col. 5. The oils actually taught were, however, paraffinic and had aromatic contents of no more than about 20%. Fuel oils are mentioned and some fuel oils have high aromatic contents. It is believed however that the fuel oils that would normally be thought of for use in practising the teaching of U.S. Patent 3,351,495 would be those that did not have high aromatic contents because of the desirability of having a flash point not much lower than 400°F (204°C) to avoid spontaneous ignition during processing under the teaching of U.S. Patent 3,351,495. Generally those fuel oils that have aromatic contents above 20% either have a flash point significantly below 400°F (240°C) or are waxes.

U.S. Patent 4,024,323 teaches the use of the plasticizers of U.S. Patent 3,351,495 in the manufacture of battery separators made from mixtures of polyolefins with other polymers, e.g. polymers of acrylic and methacrylic acid. It mentions petroleum oil as a preferred plasticizer and more specifically mineral oil is given as preferred at Col. 4 lines 14 et seq. and 61 et seq. The mineral oil given in Example 1 of U.S. Patent 4,024,323 is "Shellflex 412" which is listed in the literature as a naphthenic oil and has an aromatic content of only about 35% by weight.

German Offenlegungsschrift 2,544,303 shows in Example 4 forming a battery separator from 64% polypropylene, 11% silica and 25% polyethylene glycol plasticizer, the polyethylene glycol being extracted.

Another composition which would benefit from improvement by the present invention is that described in German Offenlegungsschrift 2,627,229. This German Offenlegungsschrift describes forming microporous films by mixing 40 to 90% by volume of a polyolefin, 10–60% inorganic filler and 30–75% of an organic liquid such as phthalic acid esters, as diethyl phthalate, dibutyl phthalate or dioctyl phthalate, fatty acid esters as the dioctyl esters of sebacic acid and adipic acid, maleic acid esters as dibutyl maleate, trimellitic acid esters as trioctyl trimellitic acid ester, phosphoric esters as tributyl phosphoric ester and octyl diphenyl phosphoric esters and glycols as polyethylene glycol and then extracting the organic liquid.

By an aspect of the invention a battery separator is provided that has an olefinic polymer as a primary binding material and a material to protect the olefinic polymer. The protective material is an oil present in an amount between about 5 to about 25%; more preferably about 8 to about 20%, of the separator weight. The oil has a high aromatic content, at least about 40% of the oil's weight, preferably about 45 to about 90%, and more preferably about 45 to about 80% of the oil's weight. The aromatic content in the battery separator, exclusive of any aromatic content in the binding polymer, is preferably about 2 to about 10% of the battery separator weight, more preferably about 4 to about 8% of the battery separator weight.

The battery separator is preferably microporous and preferably contains an inorganic filler, preferably a siliceous material, in an amount of at least about 30% of the battery separator weight. The preferred olefinic polymer is a homopolymer or copolymer of ethylene and is preferably present in an amount of at least about 20% of the separator weight. The separator is particularly advantageously for use in acid batteries.

Because of economics and viscosity, the more usual aromatic contents in the oil may be found in preferred practice to be 40 to 80% or even 40 to 70%. The high aromatic content greatly improves oxidation resistance as measured by retention of physical strength after battery life or accelerated oxidation test. In addition lower ER's (electrical resistance) are found with the preferred aromatic oil content of between 5 and 25%, especially between 8 and 20%, of the battery separator weight. The aromatic content of the oil is believed to be the primary beneficient factor in the oil and should preferably be present in the battery separator in an amount between 2 and 10% more preferably 5 and 8% of the battery separator weight. This aromatic content refers to the oil and excludes any aromatic content in the polymer of which the

separator is made.

The term "aromatic oil" when used in this application means an oil having an aromatic content of at least about 40% as determined by the ASTM procedures of the next following paragraph.

The aromatic content of the oil is determinable by ASTM method D2007 or D2549–68. In this application if the aromatic content determined by either ASTM method falls within a claimed range the content is to be understood as containing the designated aromatic content. Furthermore if either the starting oils' aromatic content or the extracted oils' aromatic content falls within a claimed range the content is to be understood as containing the designated aromatic content. The method of extraction of the aromatic content of the oil is to extract with pentane and then proceed as described in the ASTMs. Normally in the petroleum industry ASTM D2007 is preferred.

The preferred polymers are the polyolefins. Representative of polyolefins of high and low molecular weight operable in the instant invention are polyethylene, polypropylene, polybutene, polystyrene, ethylene-propylene copolymers, ethylene-hexylene copolymers, ethylene-butene copolymers, propylene-butene copolymers (including ethylene-propylene-butene terpolymers) and copolymers of ethylene or propylene with acrylic acid, methacrylic acid or both. The most preferred polymer is a homopolymer or copolymer of polyethylene and most preferably the homopolymer. Polyethylene offers both good *per se* resistance to oxidative damage in acid battery environments and good processability at economical cost. The polymer is preferably present in the finished battery separator in an amount of at least 20% of the battery separator weight. While the preferred polymer from an oxidation resistance standpoint is the homopolymer of ethylene, some copolymers of ethylene are more easily and economically processed. It is with these copolymers that the present invention is most useful because of their relatively poor oxidative resistance. The invention of the present application makes it practical to use polymers that formerly were not useful in the more oxidative battery applications as well as further enhancing the usefulness of other polymers.

The preferred battery separators contain water-insoluble inorganic fillers, for example those listed in U.S. Patent 3,351,495, Col 4, lines 9–23, and the polymer is therefore acting as a binder in such separators. The preferred inorganic filler is finely divided silica. The inorganic filler is preferably present in an amount of at least 30% of the weight of the finished battery separator.

The invention includes a process of producing a battery separator which comprises incorporating in the olefinic polymer, or coating its surface with, the aromatic oil.

It is contemplated that the oil will be supplied in the battery separator by one of two methods. In the first method the oil is incorporated in a battery separator during its manufacture, by forming a mass (composition) comprising the polymer and the aromatic oil, and typically, also a water-insoluble inorganic filler, preferably a mineral filler. A typical preferred mass comprises an aromatic oil in an amount of 10% or more of the gross weight of the mass (composition). The polymer which is preferably an ethylene homopolymer or copolymer, is preferably present in an amount of at least 10% of the mass (composition) weight with the filler being present in an amount of at least 10% of the mass weight. This mass is then formed into a sheet. Preferably the starting proportion of aromatic oil is at least 30% by weight of the mass. The oil is then extracted down to the above-mentioned proportion to provide the desired porosity in the battery separator with the remaining residual oil providing the oxidative properties desired and improved electrical resistance characteristics. At least 50% of the aromatic oil weight is usually removed from the sheet thus formed. Examples of this general procedure, but using non-aromatic oils, are given in greater detail in U.S. Patent 3,351,495 and U.S. Patent 4,024,323.

The second method for supplying the oil in the battery separator involves coating the surface of the separator, including of course the surface in the pores of the battery separator, with the aromatic oil by, for example, dipping the battery separator in an oil-solvent solution and removing the solvent, or roller-coating the battery separator with the oil, alone or mixed with diluent, or spraying the battery separator with the oil, alone or mixed with diluent. n-Hexane, hereinafter referred to merely as hexane for brevity, will usually be a suitable solvent or diluent. The starting separator could contain some aromatic oil already, e.g. less than the 5% minimum required in this invention. In this process the preferred starting battery separator comprises a homo- or copolymer of ethylene and is present in an amount of at least 20% by weight of an ethylene homopolymer or copolymer and at least 30% by weight of an inorganic filler and sufficient oil is coated to provide from 8 to 20% by weight of the oil, based on the weight of the battery separator.

Unless otherwise stated, percentages in this specification are by weight. Percentages of ingredients of a composition are based upon 100% end composition weight. Thus 10 weight percent of an aromatic oil in the battery separator means that the battery separator contains 90 weight percent of other ingredients.

The following Examples further illustrate the invention.

EXAMPLE 1

The antioxidative effectiveness of the aromatic oil was tested on "Daramic" (Trade Mark) battery separators composed essentially of polyethylene and amorphous silica made by W.R. Grace & Co., according to U.S. Patent 3,351,495. The battery separators were prepared by thoroughly washing with hexane to remove substantially all of the residual paraffinic oil, as determined by weight loss after extended extraction using a Soxhlet apparatus. The battery separators were then soaked in a 6% hexane solution of a naphthenic oil or an aromatic oil and dried to give similar oil contents, viz. 7.7 and 7.3%. (A naphthenic oil is derived mainly from cycloparaffins and is recognised as different from an aromatic oil). The naphthenic oil was "Shellflex 411" and the aromatic oil "Dutrex 357" (both products of Shell). Table 1 hereinafter shows the properties of these oils. The oil content of the separators were determined by weight difference after extended hexane extraction using a Soxhlet extraction apparatus.

The battery separators were then cut into sets of four samples 2-1/2 inch (6.35 cm.) square and subjected to electrolysis in sulfuric acid (1.400 sp. gr.) for 24 hours at 9 amps to simulate the degradative chemical effects occurring during the life of a typical lead-acid battery. This test will be referred to as "ROX" (Rapid Oxidation procedure). The ROX was carried out at the same time for all samples to obtain increased reliability of comparison. The test was repeated except the current was raised from 9 amps to 11 amps and the time was increased from 24 to 48 hours.

The tensile strength (T) and elongation (E) in the cross-machine direction was determined by die-cutting samples 0.375 inch × 2.5 inch (9.5 × 63.5 mm.) from the centre of the specimen and measuring the breaking strength and elongation at break using a tensile testing machine having a jaw gap of 1.0 inch (25 mm.) and cross-head speed of 12.0 inches (30.5 cm.) per minute. The results, set out in Table 2, show that the retention of tensile strength and elongation to break of the separator are after electrolysis very much improved by the aromatic oil.

TABLE 1
Properties of the oils (Example 1)

Properties	Napthenic oil "Shellflex 411"	Aromatic oil "Dutrex 357"
Viscosity, Saybolt Universal seconds, at 100°F	523	459
*Flash COC °F (°C)	410 (210°C)	395 (202°C)
Pour point, °F (°C)	−5 (−21°C)	35 (2°C)
Aniline point, °F (°C)	207 (97°C)	74 (23°C)
Volatility: 22 hrs./225°F (107°C) %	0.7	0.4
Clay-Gel analysis, %		
Polar Compounds	1	10
Aromatics	20	72
Saturates	79	18

*COC means "Cleveland Open Cup" Test Procedure, deseribed in ASTM D-92.

TABLE 2
The tensile strengths (T) are shown in lb./in.^{2} with conversions into kilopascals in parenthesis.

ROX 24 hrs./9amps

Sample		Before ROX T		Before ROX E	After ROX T		After ROX E	Percent Loss in T	Percent Loss in E
Naphthenic									
Sample	1	1307	(9011)	760	843	(5812)	480	35.5	36.8
	2	1241	(8556)	703	747	(5150)	341	39.8	51.5
	3	1252	(8632)	641	872	(6012)	498	30.3	22.3
	4	1352	(9322)	787	730	(5033)	369	46.0	53.1
							Average:	37.9	40.9
Aromatic									
Sample	1	1327	(9149)	569	1115	(7687)	530	16.0	6.9
	2	1351	(9315)	657	1121	(7729)	537	17.0	18.3
	3	1207	(8322)	492	1062	(7322)	504	12.0	0.0
	4	1306	(9005)	727	1099	(7577)	511	15.8	29.7
							Average:	15.2	13.7

ROX 48 Hrs./11 amps

Sample		Before ROX T		Before ROX E	After ROX T		After ROX E	Percent Loss in T	Percent Loss in E
Naphthenic									
Sample	1	1387	(9563)	642	865	(5964	388	37.6	39.6
	2	1312	(9046)	583	853	(5881)	387	35.0	33.6
	3	1357	(9356)	603	925	(6378)	381	31.8	36.8
	4	1376	(9487)	641	886	(6109)	298	35.6	53.5
							Average:	35.0	40.9
Aromatic									
Sample	1	1463	(10087)	627	1096	(7557)	356	25.1	43.7
	2	1274	(8784)	483	1049	(7233)	401	17.7	17.0
	3	1457	(10046)	598	1113	(7674)	446	23.6	25.4
	4	1392	(9598)	529	1175	(8101)	474	15.6	10.4
							Average:	20.5	24.1

EXAMPLE 2

The procedures of Example 1 were repeated except that (1) the polymer in the battery separator was a 1:1 by weight blend of polyethylene (Hercules Hifax 1900) and an ethylene-hexylene copolymer. (Allied Chemical Corp. EC 50–003), (2) the oil contents in the battery separator were different from Example 1 and (3) a ROX at 9 amps for 24 hours was used in all the tests. The details and results are shown in Table 3.

TABLE 3
The tensile strengths (T) are shown in lb./in.^{2} with conversions into kilopascals in parenthesis.

Sample Designation oil types	Oil Content %	Sample No.	Before ROX T		E	After ROX T		E	Percent Loss in T	E
Naphthenic oil of Example 1	9.6	1	946	(6522)	583	597	(4116)	256	36.9	56.1
		2	981	(6764)	578	544	(3751)	119	44.5	79.4
Polar Compound–1.3%		3	1017	(7012)	527	600	(4137)	218	41.0	58.6
Aromatic–19.9		4	944	(6509)	513	593	(4089)	135	37.2	73.7
saturates–78.8										
								Average:	39.9	66.9
Aromatic oil of Example 1	10.6	1	1038	(7157)	637	705	(4861)	333	32.1	47.7
		2	943	(6502)	563	683	(4709)	257	27.6	54.4
Polar Compound –10.0%										
Aromatics–71.9										
Saturates–18.1										
								Average:	29.9	51.1
"Tufflo 500" (product of Atlantic-Richfield Oil) a naphthenic oil	9.3	1	921	(6350)	553	584	(4027)	213	36.6	61.5
		2	907	(6254)	544	617	(4254)	246	32.0	54.8
Polar Compound–0.9%		3	937	(6460)	534	660	(4550)	306	29.6	42.7
Aromatics–41.0		4	983	(6778)	587	622	(4289)	279	36.7	52.5
Saturates–58.1										
								Average:	33.7	52.9
"Promor 503" (product of Mobil Oil) an aromatic oil	10.8	1	971	(6695)	596	752	(5185)	282	22.6	52.7
		2	983	(6778)	580	715	(4930)	237	27.3	59.1
Polar Compound–6.0		3	963	(6640)	539	720	(4964)	299	25.2	44.5
Aromatics–60.0		4	902	(6219)	502	723	(4985)	286	19.8	43.0
Saturates–34.0										
								Average:	23.7	49.8

TABLE 3 *cont.*
The tensile strengths (T) are shown in lb./in.^{2} with conversions into kilopascals in parenthesis.

Sample Designation oil types	Oil Content %	Sample No.	Before ROX T		E	After ROX T		E	Percent Loss in T	E
"Tufflo 40" (a product of Atlantic-Richfield Oil) a paraffinic oil	9.2	1	935	(6447)	584	560	(3861)	207	39.3	64.6
		2	956	(6591)	546	610.	(4205)	207	36.2	62.1
Polar Compound–1.0 Aromatics–23.0 Saturates–76.0										
								Average:	37.8	63.4

EXAMPLE 3

The procedure of Example 1 was repeated except that enough battery separators were treated for the assembly of complete batteries. The batteries were "Group 24" batteries composed of 9 regular antimonial plates per cell (4 positives and 5 negatives per cell) with 6 cells per battery. Three alternate cells were equipped with the battery separators containing the aromatic oil while the remaining cells were equipped with naphthenic oil treated separators for comparison purposes. The battery separators were subjected to the oxidative effect of the SAE life cycle test according to an adaptation of Society of Automotive Engineers Tech Report J-537f with the following results. The cold performance results (done basically as described in Tech Report J-537f) showed the aromatic oil treated separators gave 0.03 volts/cell less than the naphthenic oil treated separators (1.29 volts versus 1.32 volts respectively). The cells with the aromatic oil averaged two weeks longer (287 vs 227 cycles) on SAE life cycle. After cycling, these same aromatic oil treated battery separators showed significantly higher elongations in both the machine and cross machine directions than the naphthenic oil treated battery separators (350% vs 42% MD and 118% vs 9% CMD). Throughout testing, the aromatic oil treated battery separator cells gave cadmium voltages which were more negative, which is a desirable attribute.

EXAMPLE 4

Battery separators manufactured by Evans Products, Inc., it is believed according to U.S. Patent 4,024,323, were treated and tested as in Example 1. The untreated separators as received contained essentially no oil. The results are as shown in Table 4.

TABLE 4

	Untreated Battery Separator	Battery Separator treated with 10% of the naphthenic oil	Battery Separator treated with 10% of the aromatic oil
Tensile strength MD, lb./in.^{2}(kPa)			
Initial	947 (6529)	947 (6529)	947 (6529)
Final	0	0	324 (2234)
% Loss	100	100	66
Elongation (%)			
Initial	305 (2103)	305 (2103)	305 (2103)
Final	0	0	<10 (<70)
% Loss	100	100	>97
Tensile strength, CMD, lb./in.^{2}(kPa)			
Initial	564 (3889)	564 (3889)	564 (3889)
Final	0	0	305 (2103)
% Loss	100	100	46
Elongation (%)			
Initial	150	150	150
Final	0	0	5
% Loss	100	100	97

The beneficial effect of the aromatic oil on battery separator properties can be seen by comparing the tensile strength and elongation values of Table 4.

Experimental work to date clearly supports the view that oxidation resistance and electrical resistance are improved by the aromatic oil.

CLAIMS

1. A battery separator comprising olefinic polymer and between about 5 to about 25% of the weight of the battery separator of an oil having an aromatic contant of at least about 40% by weight.

2. A battery separator according to claim 1 wherein said oil has an aromatic content of 40

to 90% by weight.

3. A battery separator according to claim 2 wherein said oil has an aromatic content of 45 to 80% by weight.

4. A battery separator according to claim 1, 2 or 3, comprising at least 30% by weight of a water-insoluble inorganic filler, at least 20% by weight of olefinic polymer and between 8 and 20% by weight of the oil.

5. A battery separator according to claim 4 wherein the filler is siliceous.

6. A battery separator according to any preceding claim wherein the olefinic polymer is an alpha-olefin homopolymer or copolymer.

7. A battery separator according to claim 6 wherein the olefinic polymer is polyethylene or an ethylene copolymer.

8. A battery separator according to claim 7 wherein said oil has an aromatic content of 40 to about 70% by weight.

9. A battery separator according to any one of claims 1 to 6 wherein said olefinic polymer is polypropylene, polybutene, polystyrene, an ethylene-propylene copolymer, an ethylene-hexylene copolymer, an ethylene-butene copolymer, a propylene-butene copolymer, or a copolymer of ethylene or propylene with acrylic acid, methacrylic acid or both.

10. A battery separator comprising olefinic polymer and an oil and having an aromatic content exclusive of any aromatic content of said polymer, of 2 to 10% of the battery separator weight.

11. A battery separator according to claim 10 wherein said aromatic content is 4 to 8% of the battery separator weight.

12. A process of producing a battery separator claimed in claim 1 which comprises incorporating in the olefinic polymer, or coating its surface with, the aromatic oil.

13. A process according to claim 12 wherein a composition comprising an olefinic polymer and at least 10% by weight of an oil having an aromatic content of at least 40% by weight is formed into a battery separator.

14. A process according to claim 13, wherein the starting composition comprises at least 10% by weight of an ethylene homopolymer or copolymer, at least 10% by weight of a water-insoluble inorganic filler and at least 30% by weight of the oil, and after the composition has been formed into a sheet, at least 50% by weight of the oil is removed.

15. A process according to claim 12 wherein the surface of a battery separator of olefinic polymer is coated with sufficient aromatic oil to provide 5 to 25% of the oil, by weight of the separator produced.

16. A process according to claim 15 wherein the battery separator comprises a homo- or copolymer of ethylene and is present in an amount of at least 20% by weight of an ethylene homopolymer or copolymer and at least 30% by weight of an inorganic filler and sufficient oil is coated to provide from 8 to 20% by weight of the oil, based on the weight of the battery separator.

17. A process according to claim 12, 13, 14, 15 or 16 wherein said oil has an aromatic content of 40 to 90% by weight.

18. A process according to claim 17 wherein said oil has an aromatic content of 45 to 90% by weight.

19. A process according to claim 18 wherein said oil has an aromatic content of 45 to 80% by weight.

20. A battery separator produced by a process claimed in any one of claims 12 to 19.

21. A battery separator according to claim 1, substantially as described in any one of the Examples.

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